Abstracts of the physico-chemical literature in Japan

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL
(STRUCTURE—PROPERTIES—REACTIONS)

Light figures in single crystals of iron and aluminium. M. Yamamoto. *Nippon Kinzoku Gakkai-Si*, 5, 324—333 (1941).—Single crystals of iron and aluminium were prepared by the method of recrystallization and etched for different time-intervals with aq. solns. of various concns. of acids and salts. Light figures produced when a pencil of light was allowed to fall on their three principal crystal planes (100), (110), and (111) were observed and photographed, and the suitability of the observed figures for detmg the orientation of the said metal crystals with the "method of light figures" was examd. As found in the previous investigation of light figures in single crystals of nickel and copper, the symmetry characteristics of the light figures are naturally invariable, but their geometrical form changes with the etching reagent and the time and temp. of etching. Clear light figures were observed on (100) planes by a short-time etching of several minutes, namely, the light figures suitable for the detn. of the crystal orientation were obtained, in cases of iron single crystals etched with concd. nitric acid and hydrochloric acid, dilute (10 and 20 percent) solns. of ammonium persulphate, and 70 percent soln. of ferric chloride, and also in cases of aluminium crystals etched with concd. *aqua regia* and hydrochloric acid, and 10 percent soln. of ferric chloride. Author.

Studies on the hydrates of aluminates of alkaline earth metals. I. The constitution of the hydrates of barium aluminate. G. Maekawa. *J. Soc. Chem. Ind. Japan*, 44, 912–15 (1940).—The author examd. the dehydration curves of the hydrates of barium aluminate, $BaOAl_2O_3 \cdot 6H_2O$, $2BaOAl_2O_3 \cdot 5H_2O$ and $3BaOAl_2O_3 \cdot 7H_2O$. From the result, the author proposes the following chem. structure for these three kinds of hydrates of barium aluminate—$Ba[OAl(OH)_2]_2 \cdot 4H_2O$, $Ba[OAl(OH)_2]_2[Ba(OH)_2] \cdot 2H_2O$ and $Ba[OAl(OH)_2]_2[2Ba(OH)_2] \cdot 3H_2O$. These hydrates were formerly considered as monobasic, dibasic and tribasic resp. But the formulas proposed by the author indicate that these hydrates are the double salts of $Ba[OAl(OH)_2]_2$ and $Ba(OH)_2$. They dissociate, therefore, in aq. soln. into $Ba[OAl(OH)_2]_2$ and $Ba(OH)_2$. $Ba[OAl(OH)_2]_2$ exhibits itself as a salt of a monobasic acid. Author.

Molecular compounds of alkyl tin halides. T. Harada. *Sc. P.*, 38, 146–166 (1940).—The action of sunlight upon R_3SnX and the formation mechs. (A) of $[((CH_3)_3Sn\,OH)_2Sn(CH_3)_3]X$, $[((C_2H_5)_3SnOH)_2Sn(C_2H_5)_3 \cdot H_2O]X$ and (B) of $[R(R_2SnO)_3OH \cdot SnR_2X_2]$ are investigated. The formation (A) or preparations and the properties of R_3Sn- and R_2Sn radicals and their compds. are reinvestigated in connection with the study on their formation. The relation between the yield of R_4Sn and the compn. of alloys of the

system Sn—Na—Zn for alkylation of Sn with RX is described. R_3Sn^- is isolated (1) by $2R_3SnX+2Na=(R_3Sn)_2+2NaX$ and (2) by $(R_2SnNa)_2+2RX=(R_3Sn)_2+2NaX$. R_2Sn is prepared by $R_2SnX_2+2Na=R_2Sn+2NaX$ in liquid NH_3 as an orange-yellow solid. $((CH_3)_3Sn)_2O$ is prepared according to $2(CH_3)_3SnOH+Na=((CH_3)_3Sn)_2O+NaOH+\frac{1}{2}H_2$ in benzene soln. $(CH_3)_3SnX$ unites with $((CH_3)_3Sn)_2O$ directly to form $[((CH_3)_3Sn)_2O\cdot Sn(CH_3)_3]X$ which can therefore be regarded as a derivative of the hypothetical $H_3O\cdot OH$. R_3SnX also combines with R_3SnOH in the ratios 1:1 and 1:2 forming $[(CH_3)_3SnOH\cdot Sn(CH_3)_3H_2O]Cl$ and $[((CH_3)_3SnOH)_2Sn(CH_3)_3]X$, and $[((C_2H_5)_3SnOH)_2Sn(C_2H_5)_3H_2O]X$. R_2SnX_2 and $R_2Sn(OAc)_2$ exhibit a similar behavior with R_2SnO or $R_2Sn(OH)_2$ by combining in the ratios 1:1, 1:2 and 1:3 to form $[R_2SnO\cdot SnR_2X_2]$, $[R_2SnOSnR_2O\cdot SnR_2X_2]$, $[R_2SnOSnR_2OSnR_2O\cdot SnR_2(OAc)_2]$, $[R'OSnR_2OSnR_2OSnR_2OR'\cdot SnR_2X_2]$ (R'=alkyl radical or H of its solvent alcohol or H_2O. The mechs. of formation (A) are represented as $2R_3SnX \xrightarrow{light} (R_3Sn)_2+X_2$, $(R_3Sn)_2+\frac{1}{2}O_2\rightarrow (R_3Sn)_2O$. $X_2+R_4Sn\rightarrow R_3SnX+RX$, $(R_3Sn)_2O+R_3SnX\rightarrow[(R_3Sn)_3O]X$, then by H_2O it is converted thus: $[(R_3Sn)_3O]X+H_2O\rightarrow[(R_3SnOH)_2SnR_3]X$, or $(R_3Sn)_2O+H_2O\rightarrow 2R_3SnOH$, $2R_3SnOH+SnR_3X\rightarrow[(R_3SnOH]_2SnR_3]X$. The formation of the ethyl compd. is likewise but forming $[((C_2H_5)_3SnOH)_2Sn(C_2H_5)_3H_2O]X$. In the formation of B from R_3SnX it first produces $(R_2Sn)_2O$ or $R_2Sn(OH)_2$ and HX through the formations of $(R_3Sn)_2O$ and R_3SnOH. These compds. then interact with each other and finally form the compd. in question according to $R_2SnO+2HX\rightleftarrows R_2SnX_2+H_2O$, $R_2SnX_2+2H_2O\rightleftarrows R_2Sn(OH)_2+2HX$, $R_2Sn(OH)_2+R_2Sn(OH)_2\rightarrow HOSnR_2OSnR_2OH+H_2O$, $HOSnR_2OSnR_2OH+R_2Sn(OH)_2\rightarrow HOSnR_2OSnR_2OSnR_2OH+H_2O$, $HOSnR_2OSnR_2OSnR_2OH+R_2SnX_2\rightarrow[HOSnR_2OSnR_2OSnR_2OH\cdot SnR_2X_2]$. Author.

On the theoretical intensity curves of the three halos obtained from thin films of organic substances in amorphous state by electron diffraction. J. Kakinoki. *Proc. Phys-Math. Soc. Japan*, **23**, 666-667 (1941).—Thin films of org. substances in amorphous state such as cellulose, its derivatives, polystyrene, agar, gelatin, etc., were found to give practically the same three halos by electron diffraction. Their positions are $s_1=1.39$, $s_2=3.12$ and $s_3=5.30$ where $s=\frac{4\pi}{\lambda}\sin\frac{\theta}{2}$. A good agreement of the theoretical intensity curve with the observed result was obtained when the calcn. was made by using such formula as

$$I(s)\propto\left\{\sum_{r_{ij}=1.5}Z_iZ_j\frac{\sin s\,r_{ij}}{s\,r_{ij}}+\sum_{r_{ij}=2.5}Z_iZ_j\frac{\sin s\,r_{ij}}{s\,r_{ij}}+4\pi\varphi c\int_l^\infty\frac{r^2\sin sr}{sr}\,dr\right\}.$$

In this formula, the first and the second summations are performed over the range of $r_{ij}<3.0$ for the cellobiose model given by Meyer and Misch and in the last integral, φ means the mean scattering power (about 48), c a const. concerning the density and chemical formula of cellulose and l is the minimum value of the longer distances contributing to the inner halo (l is about 3.5 A). This expression of I(s) gives three maxima the s-values of which are about 1.5, 3.4 and 5.3 being in good agreement with the observed values. There seem to be some errors in the calcn. made by Kargin and Leypunskaja (*Acta Physicochimica, U.R.S.S.* **XII** (1940), 397.) for the same cellobiose model.

Author.

A brief report on the crystal structures of some thiuram type accelerators. T. Yamada and K. Mizuno. *J. Soc. Chem. Ind. Japan*, **44**, 304B (1941).—The thiuram type accelerators are well known as the ultra rapid accelerators for the vulcanization of rubber. The good crystal of tetramethylthiuram monosulfide (I) and disulfide (II) was obtained from benzene soln. The goniometric measurement and X-ray

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analysis were used. The space group of (I) is $C_{2h}^5-P2_1/a$; and there are 4 mols. in a unit cell of the following dimensions, $a_0=13.99$Å, $b_0=7.47$Å, $c_0=10.22$Å, $\beta=110°27'$. The minimum molecular symmetry is C_1-1. The crystal cleaves along the (100) plane. In the case of (II) the space group is C_{2h}^6-A2/a; and there are 4 mols. per cell. The monoclinic unit has $a_0=13.94$Å, $b_0=9.93$Å, $c_0=9.64$Å, $\beta=123°27'$. The molecule of (II) is at least the symmetry of $C_i-\bar{1}$ or C_2-2. The crystal of (II) frequently crystallizes in contact twin form, the twin face being (100) plane.

The molecular symmetries of the two compds. as disclosed by the present investigation suggest that the valence angles of the sulphur atoms in these molecules differ from 180°, as expected. The complete structure analysis is in progress. Authors.

Studies of synthetic fiber. V. Viscosity formula of polyamide. 2. K. Hosino. *J. Chem. Soc. Japan*, **62**, 602–608 (1941).—Number-average molecular wt. of low-degree polymerized polyhexamethylene adipamide was measured by means of freezing point depression method of phenolic soln. of the same polymer. Applying Flory's theory on condensation polymer, wt.-average molecular wt. Mw was calcd. and the following relations were found between intrinsic viscosity $[\eta]$ and Mw:

$$[\eta]_{20}=5.9\cdot10^{-5}\mathrm{Mw}+0.09$$
$$[\eta]_{25}=5.4\cdot10^{-5}\mathrm{Mw}+0.085$$
$$[\eta]_{30}=5.1\cdot10^{-5}\mathrm{Mw}+0.08$$

These formulae are derived from Eisenschitz, Kuhn, and Guth's eq.:

$$[\eta]=\frac{\varphi_*}{1600}\left(\frac{l}{d}\right)^2+\frac{2.5}{100}\varphi.$$

Some discussions are given on the equil. const. of condensation and rate of reaction of polyamide formation. Author.

Sulphuration of the surface of polished silver. R. Ueda. *Science*, **11**, 482 (1941).—The surface of polished silver is made black by passing H_2S gas on it. The examn. by diffraction of cathode ray shows that the diffraction image obtained is in agreement with that of acanthite which is one of the Ag_2S crystals. Other specks are also observed, which may be due to the presence of an unknown silver sulphide. J. C. L.

Polarity and molecular structure of diphenylene dioxide. K. Higasi and S. Uyeo. *J. Chem. Soc. Japan*, **62**, 396–399 (1941).—The dipole moments of some derivatives of diphenylene dioxide were detd. by the dilute soln. method with the following results: diphenylene dioxide 0.64 D in benzene and 0.57 D in hexane, 2.6-dimethyldiphenylene dioxide 0.61 D in benzene, and 2.6-dichlorodiphenylene dioxide 0.62 D in benzene. From these results it is concluded that diphenylene dioxide has a folded configuration about the O—O axis. Considering the heat of activation in the racemization reaction it is shown that molecule is so flexible about the O—O axis that no optical isomers can exist.

Authors.

The vapour pressures of some molecular crystals. II. S. Seki. *J. Chem. Soc. Japan*, **62**, 789–795 (1941).—By means of the same method as in the previous report, the vapour press. of CBr_4, $TiBr_4$, $SnBr_4$, and SnI_4 were measured in the crystalline as well as in the liquid phase. From these data the changes of thermodynamic quantities, $\triangle H$, $\triangle F$, $\triangle F_{298.1}$, and $\triangle S_{298.1}$ for the phase change were calcd. The transition point of CBr_4 (ca. 46°C) already reported was not observed from the vapour press.-temp. curve. It is reported that such is also found in the case of crystalline CCl_4. On this point further investigation is necessary. The values of $\triangle H$, etc., were very similar for $TiBr_4$ and $SnBr_4$, and the heats of fusion of these substances were reasonable as compared with the results of direct measurement of other authors. For SnI_4 the heat of fusion and the vapour press. were somewhat different from the data reported by Negishi. Author.

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The vapour pressure of molecular crystals. III. S. Seki and I. Nitta. *J. Chem. Soc. Japan*, 62, 907–914 (1941). The vapour press. of crystalline and liquid $C(NO_2)_4$ was measured. From this some thermodynamic quantities were calcd. The Trouton and the Hildebrand consts. were computed and compared with those of many other liquids of the type AB_4 measured by the present authors. From these consts. and entropy change of fusion, $C(NO_2)_4$ was found to be a sort of abnormal liquid. According to the statistical-mech. theory of liquid by Eyring some physical consts. for intermolecular forces and the free volumes of liquids of the AB_4 type were calcd. and it was concluded that such liquids are apparently normal. Also the computed thermal expansion coeff. and compressibility at const. press. showed fairly good agreement with the values from Saslawski's empirical formula and also with the direct exptl. values. Authors.

Über den Quellungsgrad und die Löslichkeit des Polyvinylalkokols. S. Okamura und S. Kawasaki. *J. Soc. Chem. Ind. Japan*, 41, 950–953 (1941).—Um das in warmem Wasser lösliche Polyvinylalkokol in unlösliche Produkte überzuführen, wird dieses auf höhere Temperaturen erhitzt oder nach der Erhitzung ferner mit Formaldehyd teilweise acetalisiert. Dieses letzte Verfahren wurde von S. Lee und Mitarbeiter für die Herstellung von hochwertigen reinsynthetischen Fasern aus Polyvinylalkokol verwendet. In der vorliegenden Untersuchung wurden der Quellungsgrad und die Löslichkeit des Polyvinylalkokols, in Form von Film, vor und nach der obigen Behandlungen verglichen.

Wie aus der Resultate hervorgeht, nimmt das Quellungsgrad durch Erhitzung stark ab. Acetalisierung mit Formaldehyd übt fast keinen grossen Einfluss auf die Quellung aus, während die Quellbarkeit durch Acetalisierung mit Acetaldehyd stark abnimmt.

Authors.

The separation of iso- and normal butyl alcohols from hydrocarbons by azeotropic distillation. R. Negishi and C. Isobe. *Bull. C. S. J.*, 16, 278–284 (1941). —By use of the principle of azeotropic distillation, iso- and normal butyl alcohols have been separated, respectively, from their binary mixts. with toluene. The individual alcohols have been also separated from a mixt. consisting of the alcohols and commercial gasoline. This method has been found quite simple and fairly accurate. The actual loss of the alcohol is independent of its content in the mixt; in other words, the loss is chiefly mech. and operational. For a mix. cont. 5cc of alcohol, its percentage error in the final result is about 5; for 10 cc, it is about 3; and for 15 cc or larger, it is approximately 1 or even less. Water has been used as the azeotropic forming substance in this method.

Authors.

The synthesis of iso- and normal butyl alcohols in the presence of calcium carbide. R. Negishi. *This Journal*, 15, 171–181 (1941).

Studies on calcium carbide. I. Preparation of pure calcium carbide. N. Kameyama and Y. Inoue. *J. Soc. Chem. Ind. Japan*, 44, 825–828 (1941).—In order to prepare the calcium carbide pure enough to be used for the detn. of physico-chem. const., the four different methods were tried. I. Calcium-liquid ammonia method. Crystals of $CaC_2{\cdot}C_2H_2{\cdot}4NH_3$ were prepared by passing C_2H_2 into the liquid ammonia soln. of metallic calcium, and they were separated and heated gradually, evacuating the gases evolved. Pure carbide can be produced if excess of acetylene be carefully avoided; otherwise, resinous compds. are produced by the polymerisation of acetylene or its derivatives. The carbide prepared by this method is white powder, very reactive, and, when it comes into contact with the air, it is immediately oxidised, liberating free carbon. Thrown into water, it evolves acetylene so violently that free carbon is separated by the

exothermic decompn. of acetylene. Thus being too reactive due to its powdery form, the product of this process is not suitable for the purpose of the present investigation. II. Lime-carbon method. The product of about 97% of purity can easily be obtained from a mixt. of lime and sugar charcoal in the ratio CaO : 3C by heating at about 1700°C for less than an hour keeping the gaseous press. at about 100 mmHg. Failing the optimum of conditions of heating, this method is apt to give a product containing free carbon, owing to the evaporation of calcium, either by the dissocn. of the carbide once formed or by the direct reaction of CaO+C into Ca+CO. III. Cyanamide-carbon method. The reaction is as follows:— $CaCN_2+C=CaC_2+N_2$. Pure $CaCN_2$ was prepared by Kameyama's method, that is the repeated heating of CaO with dicyanodiamide $(CN_2H_2)_2$ and was mixed with sugar charcoal or wood charcoal and the mixt. was compressed into cakes, which were heated in a vacuum furnace, preferably at 1150°C for the first 2 hours under 2 mmHg of press. and later at 1250°C for 1 hour under 2~40 mmHg of press. The product of more than 98% purity was thus obtained. IV. Cyanamide method. Cakes of pure $CaCN_2$ were heated in a vacuum furnace at about 1100°C for the first 3 hours and later at about 1200°C for 2 hours, all under a few millimeter of press. The product was of about 97~98% purity. The products of both the methods III. and IV. are white, pure, and as they are of cake form, are suitable for handling. The last two methods are suitable for the present purpose.

Authors.

Studies on the reactions between oxides in solid state at high temperatures. I. The reaction between magnesium oxide and titanium oxide. Y. Tanaka. *Bull. C. S. J.*, **16**, 428–441 (1941).—It is confirmed that three titanates, i. e., magnesium orthotitanate ($2MgO\cdot TiO_2$), metatitanate ($MgO\cdot TiO_2$) and dititanate ($MgO\cdot 2TiO_2$), are formed by the solid reaction between MgO and TiO_2. $2MgO\cdot TiO_2$ is soluble in 4N HCl and $MgO\cdot TiO_2$ in 12N HCl, while $MgO\cdot 2TiO_2$ is scarcely soluble even in 12N HCl. By following the course of the reaction analytically, it is found that the first reaction product is $MgO\cdot 2TiO_2$, whatever the mixing ratio of the two components may be: $MgO\cdot TiO_2$, is formed gradually when an excess of MgO is present; and $2MgO\cdot TiO_2$ is formed similarly, but with difficulty. The reaction proceeds in the same manner under various experimental conditions, and $MgO\cdot TiO_2$ can never be regarded as the first reaction product. The reaction between $MgO\cdot TiO_2$ and TiO_2 to form $MgO\cdot 2TiO_2$ takes place more easily than the formation of $MgO\cdot TiO_2$ from $MgO\cdot 2TiO_2$ and MgO. Although there exists a notable rapid initial reaction, a further reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process of $MgO\cdot 2TiO_2$ formation is estimated to be 36.0 Kcal per mole. J. C. L.

Investigations on the manufacture of acetaldehyde from acetylene. I. Experiments on the velocity of absorption of acetylene by hydration liquid. S. Ueno and Y. Orito. *Repts. of the Imperial Industrial Research Institute, Tokyo, Japan*, **36**, 1–25 (1941).—20% sulfuric acid contg. about 7% ferric sulfate and small quantity of mercuric sulfate, was circulated by a specially devised stirrer along the inner surface of a cylindrical reaction vessel, immersed in a thermostat. The stirrer is made of a Y-shaped glass tube which can rotate rapidly around its symmetrical axis and the sulfuric acid soln. is forced to flow through this tube by the centrifugal force generated by the rotation. In this manner cylindrical liquid film flowing down the surface of the vessel is formed, and the absorption area of the liquid is extensively increased. Acetylene gas was passed in at const. rate into the vessel and the volume absorbed was detd. by observing the volume of the entering and

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escaping gas by means of a gasometer and correcting it to the standard condition. At the beginning of the reaction the absorption velocity was low, but it increased gradually till a stage was reached in which the absorption proceeded at a const. speed for some period. The absorption velocity at this stage was measured at various mercuric sulfate concns. and also at various ratios of the absorption area and the volume of the hydration liquid, and the results being summarized, the following empirical formula expressing the absorption velocity of acetylene was obtained:

$$(\Delta V/\Delta t)_m = A[1 - 1/\{1 + (B.V_l.C)/(A.S)\}]$$

where $(\Delta V/\Delta t)_m$ is the absorption velocity at the stage above described, S is the absorption area, V_l is the volume of the hydration liquid, C is the concn. of the mercuric sulfate, A and B are both consts. **II. Theoretical formula expressing the velocity of gas absorption by liquid due to chemical reaction, and consideration on the order of the hydration reaction of acetylene.** *ibid.*, **36**, 17–25 (1941).—When a gas is absorbed by a chem. reaction, the quantity of the gas absorbed must be equal to that consumed in the liquid, and the velocity of absorption, according to the diffusion film theory, must obey Fick's law. If we consider the case where the reaction is of 1st order with respect to the gas, and the concn. of the reaction component in the liquid can be assumed to be equal in all parts of the liquid, and moreover the concn. of the gas in the inner part of the liquid is maintained same by stirring, then the absorption velocity, from the standpoint mentioned above, should be expressed by the following theoretical formula:

$$dW/dt/S = k_l \cdot C_0 \cdot \frac{\alpha d}{\tanh \alpha d}\left[1 - 1/\cosh^2 \alpha d\left\{1 + \frac{V_l \cdot k_c \cdot \tanh \alpha d}{S \cdot k_l \cdot \alpha d}\right\}\right]$$

where dW/dt is the absorption velocity of the gas, S is the absorption area, C_0 is the gas concn. at the absorption surface of the liquid, d is the thickness of the diffusion film, $k_l = D/d$ where D is the diffusion const. of the gas in the liquid, α is the square root of k_c/D where k_c is the reaction velocity in the liquid in which the gas concn. is unit, and V_l is the volume of the liquid. The above formula can be simplified according to the magnitude of αd, thus: (i) $\alpha d < 0.5$, $dW/dt/S = k_l C_0\{1 - 1/(1 + V_l k_c/S k_l)\}$; (ii) $0.5 < \alpha d < 2$, $dW/dt/S = k_l \cdot C_0 \cdot \alpha d/\tanh \alpha d$; (iii) $\alpha d > 2$, $dW/dt/S = k_l C_0 \cdot \alpha d = C_0\sqrt{D \cdot k_c}$. If the reaction is of 1st order with respect to both acetylene and mercury, the coincidence of the theory and expt. can be concluded. Authors.

2—SUB-ATOMICS, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Scattering of neutrons by proton. T. Wakatuki and K. Husimi. *Proc. Phys.-Math. Soc. Japan*, **III**, **23**, 855–860 (1941).—The scattering of neutrons by proton is theoretically a spherical symmetry. Dee and Gilbert, however, do not think so. The present authors observed the angular distribution of the scattered neutrons by means of a Wilson chamber. 1027 tracks chosen gave a slight indication that it is asymmetry. It is emphasized that more than 10,000 tracks will have to be analysed to get a decisive conclusion. J. C. L.

On the relative cross sections of the (n, α) and (n, p) reactions produced by fast neutrons. T. Amaki and A. Sugimoto. *Sc. P.*, **38**, 377–381 (1941).—Using the induced radioactivities, the relative cross sections of the (n, α) and (n, p) reactions

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caused by fast neutrons were studied for some elements lighter than Zn. J. C. L.

Contribution to the molecular theory. T. Takeuti. *Bull. Tokyo Univ. Eng.*, **10**, 327–329 (1941)—The mechanism of thermal conduction in solids is outlined and the compressibility is discussed.

Author.

On frozen light. T. Takeuti. *Bull. Tokyo Univ. Eng.*, **10**, 330–331 (1941).—The so-called frozen light was experimented with zinc sulphide and common salt and was theorized. Author.

Absorption spectra of metallic complexes. VII. Absorption spectra of copper-ammonia complexes and structure of these complex radicals. M. Kubota. *J. Chem. Soc. Japan*, **62**, 509–515 (1941). — The third absorption bands of copper-ammonia complexes were found. This proved the existence of the complex radical whose structure is trans negative, such as $\left[Cu(NH_3)_4(OH)_2\begin{pmatrix}(1)\\(6)\end{pmatrix}\right]$ in soln. In the case of high concn. of ammonia, this band disappears. Namely in high concn. of ammonia, such complexes as $[Cu(NH_3)_5OH]^+$, $[Cu(NH_3)_6]^{++}$ are formed. The absorption bands of two shelled complexes, $[[Co(NH_3)_6](SO_4)_3]^-$ and $[[Cu(NH_3)_6](SO_4)_3]^-$, were observed.

Author.

Absorption spectra of cobalt bromide solution. Y. Hukumoto and S. Kobayashi. *The Science Reports of the Sendai Higher Technical School.* **14**, 16–22 (1940). —In this expt., hydrobromic acid soln. of cobalt bromide was used. By changing the concn. of the acid gradually from 0.73 N to 7.24 N, the colour of the soln. turns from red to blue: the concn. of 5.98–5.48 N appears to the naked eye to be the transition point. According to the observation by the photometer, however, the change of the red part is remarkable, and in this long part of the long wave, a noteworthy change of colour of the three degrees is observed, that is, the coeff. of extinction, which is level at 2.5 N HBr, suddenly rises, and runs parallel to the concn. axis at about 5N again. If the part of the rising steep inclination is extended, it intersects with the concn. axis at about 3.5 N. The ratio of Br atoms at three critical concns. 2.5 N, 3.5 N, 5 N of HBr, corresponding to the changes of these three-degrees, to the H_2O molecules is 2:3:4, and is identical with the ratio of numbers of Br atoms in a complex compd. explained by the theory of hydro complex radical.

Authors.

Studies on the near ultraviolet absorption spectra of benzene and its derivatives. III. Phenol. K. Asagoe, Y. Shimokawa and S. Kageyama. *Jap. Journ. Phys.*, **14**, 11–16 (1941).—Phenol has a weak absorption in the region from 2500Å to 2800Å. The absorbing power of phenol is estimated to be more than 230 times as strong as that of benzene. A. L. Sklar's theoretical value (20 times) seems to be too small as compared with our exptl. one. The phenol molecule, although O—H bond is not parallel to C—O bond, has the vibrational structure quite similar to those of the halogen derivatives of benzene. This shows apparently that the phenol molecule may be considered as having an axial symmetry as in the halogen derivatives, owing probably to the small mass of the H-atom. Const. frequencies namely 779(*c*), 932(*d*), 982(*b*), 473(*a*) and 1272 cm^{-1} are most frequently observed. These may probably be considered as the totally symmetrical vibration frequencies in the upper state corresponding to 813, 1002 (or 1024), 1024 (or 1002), 614 and 1253 cm^{-1} in the lower state resp. Two or three overtones and combinations of these frequencies are also found. Several 220 and 60 cm^{-1} progressions were found on the longer wavelength side of each of these main bands. These may be interpreted as due to series of the $n \rightarrow n$ transitions of low frequency nontotally symmetrical vibrations. The 60 cm^{-1} progressions

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may tentatively be attributed as concerned with the Raman frequency 235 cm^{-1} and 220 cm^{-1} ones with 526 cm^{-1}. **IV. Aniline.** *Proc. Phys.-Math. Soc. Japan*, **3**, 23, 820–828 (1941).—The absorption spectrum of aniline is found in the region from 3000Å to 2600Å. The absorbing power is estimated to be more than 620 times as strong as that of benzene. The value given by A. L. Sklar theoretically is 140. The vibrational structure of the band is also similar to those of the halogen derivatives of benzene. The aniline molecule may thus probably be regarded as having an axial symmetry at least with respect to the vibration phenomena. Const. frequencies 490(*a*), 950(*b*), 795(*c*) and 1300(*e*) cm^{-1} are considered as those of the totally symmetrical vibration frequencies in the upper state corresponding probably to 617,996, 822 and 1601 (1272)cm^{-1} in the ground state resp. Several overtones and probable combination tones of these frequencies are also found. Just similarly to the other monoderivatives of benzene, as the series of $n \rightarrow n$ transitions of low frequency nontotally symmetrical vibrations, 40 and 230 cm^{-1} progressions in the longer wavelength side of each of the main bands are observed. The 40 cm^{-1} progressions may tentatively be attributed as concerned with the Raman frequency 234 cm^{-1}, while the 230 cm^{-1} ones with 532 $cm.^{-1}$ Thus the upper states corresponding to these become 194 and 302 cm^{-1} resp. In aniline, however, is found another similar system of bands shifted towards the shorter wavelength side from the above mentioned system by about 294 $cm.^{-1}$ No spacing similar to the 294 cm^{-1} is observed in the other monoderivatives of benzene. The authors are inclined to interpret this frequency as corresponding to the twisting vibration of the NH group about C–N (or $C=N^+$) bond in the excited state. That is, there may exist in the excited state two forms of aniline molecule, namely plane and perpendicular just similarly to the ethylene molecule. **V. Fluorobenzene.** K. Asagoe and Y. Ikemoto. *Proc. Phys.-Math. Soc. Japan*, **3**, 23, 829–834 (1941).—A weak absorption spectrum of F-benzene is observed in the region from 2740Å to 2440Å. The absorbing power estimated is about 27 times as strong as that of benzene. This value is about 10 times as large as that reduced theoretically by A. L. Sklar. Similarly to the preceding monoderivatives, const. frequencies of 778(*c*), 919(*d*), 965(*b*), 1224(*e*) and 515(*a*) cm^{-1} are observed. Several overtones of these frequencies and probable combination tones with one another are also found. Thus the above mentioned frequencies may be regarded as of the totally symmetrical vibrations in the upper state. 515 and 778 cm^{-1} may correspond to 610 and 802 cm^{-1} in the lower state resp. 919 and 965 cm^{-1} are considered as corresponding to 1001 and 1160 cm^{-1} (or in the reverse order) resp. 1224 cm^{-1} seems to correspond to 1600 or 1218 cm^{-1} in the lower. As the series of $n \rightarrow n$ transitions of low frequency nontotally symmetrical vibrations, two progressions of 67 and 209 cm^{-1} spacings are observed. These may be concerned with the Raman frequencies 239 and 518 cm^{-1} resp., corresponding frequencies in the upper state being estimated as 172 and 309 cm^{-1} resp. Authors.

Dependence of photo-sensitivity of the semitransparent photo-cathode, Cs–Cs_2O, Cs. Ag–[Ag], on the film thickness and the scattering of light by the film. S. Hirai, *Mazda Kenkyujiho* **16**, 379–383 (1941).—Thin, wedge-shaped silver film was prepd. by evaporation of silver in high vacuum on the inner wall of a cylindrical glass tube which was previously baked out sufficiently in vacuum, and its electric conductivity, and transmission, reflection and scattering of light were measured at different thicknesses. Without exposing the film to the air, a semi-transparent caesium photocathode was made with the silver film by the usual method, that is, by oxidising the film by discharging through oxygen gas and then depositing caesium into it. By the measurements of photo-sensitivity of the surface illuminated from vacuum and glass sides,

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the following results were obtained. i. The photo-sensitivity when illuminated from the glass side is proportional to the transparency of the film unless its resistivity is very large. ii. When the silver film is so thin (thinner than about 15 mμ) that it shows scattering of light, the sensitivity of the cathode when illuminated from the glass side is greater than that from the vacuum side. The difference amounts to 50% of the former. This phenomenon is believed to be related to the scattering of light by the colloidal metal particles in the composite photo-cathode.

Author.

Optical rotatory power and circular dichroism I. Measurement of rotatory dispersion in the ultra-violet. M. Kobayashi. *J. Chem. Soc. Japan*, **62**, 884—887 (1941). The method of using an app. similar to the one used by Kuhn is described for the measurement of the natural rotatory power in the visible and near ultra-violet regions, and rotatory dispersions of quartz and d-tartaric acid are accurately detd. down to 2400Å.

Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY
(THERMODYNAMICS)

Studies on air-depolarised cell. I. Theoretical consideration of diffusion of atmospheric oxygen in the porous carbon electrode. K. Takahashi. *J. Electrochem. Assoc. Japan*, **9**, 209–219 (1941).— The principle of air-depolarized cell is to let atmospheric oxygen diffuse through a porous carbon electrode used as catalyst in order to let it reach the surface where depolarisation takes place and electro-motive force is generated. During the cell action, oxygen diffuses first into the porous carbon electrode from its surface exposed to atm. then it is adsorbed by the surface of individual carbon grains that composing the electrode, and further the molecule is changed into OH^- ion and dissolved into the electrolyte. During the inactive period, the cell is recovered by the carbon layers adsorbing atmospheric oxygen to supply the concn. difference caused by the disparity between the oxygen consumed and that diffused in the carbon electrode. The author advanced a theoretical consideration of the diffusion of oxygen into the electrode: it is assumed that one end surface of it is always exposed to atm. and that diffusion process takes place in one direction (x-axis) only, namely, the equiconcn. surfaces are assumed to be planes parallel to the exposed face. Then the problem may be dealt with simply in one-dimensional, and furthermore, it is assumed that the carbon, having previously adsorbed air, is in the state of equil. with atm.: temp. and press. are considered const. throughout the system. Based upon the above assumptions, the fundamental eq. of diffusion may be expressed as follows:

Case I. Discharge State

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2}-Ki$$

Boundary conditions are,

$$C=C_0 \quad \text{at} \quad x=0$$

$$\frac{\partial c}{\partial x}=0 \quad \text{at} \quad x=1$$

$$C=C_0 \quad \text{at} \quad t=0$$

Case II. Rest State

$$\frac{\partial c'}{\partial \theta}=D\frac{\partial^2 c'}{\partial x^2}$$

Boundary conditions are,

$$C'=C \quad \text{at} \quad x=0$$

$$\frac{\partial c'}{\partial x}=0 \quad \text{at} \quad x=1$$

$$C'=C \quad \text{at} \quad \theta=0$$

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where K=const. D the diffusion coeff., l the length of electrode, i the current density (Amp./gr. depolariser), C & C′ the concn. state of oxygen t & θ the time during discharge and rest states resp. Under certain assumptions, by solving these eqs. (the complete solution is given in the original paper) concn. distribution, diffusion velocity, diffused quantity and time relation are derived. Also discussions are made about the effects of various factors. Finally, some comments are given about the comparison of the above results with the adsorption velosity eq. of gases on porous substances hither-to proposed. Author.

Standard electromotive force of the cell with mixed solvents and the salting-out effect. S. Kaneko. *Bull. Electrotech. Lab.*, **6**, 499–501 (1941).—The standard electromotive force of the cell with mixed solvents is calcd. from thermodynamics and Debye's theory of salting-out effect. Author.

The effect of chlorine on the electrolytic refining of copper. K. Anazawa and T. Kakiyama. *J. Electrochem. Assoc. Japan*, **9**, 163–169 (1941).—The results obtained by the electrolysis of copper sulphate with the addition of common salt or hydrochloric acid are as follows: (1) Polarization potential on anode is approximately doubled by the addition of 5 mg./L of Cl′, but is not further affected by any more addition. (2) The addition of 5–10 mg./L. of Cl′ raises the polarization potential on cathode distinctly, while a further addition reduces the rate until at a greater amount than 50 mg./L. a gradual fall ensues. (3) There is no difference between the effects of common salt or hydrochloric acid on polarization potential. J. C. L.

Determination of the vapour pressures of solid salts. IV. Vapour pressures of WO_3, MoO_3, CdO and TeO_2, and calculation of their thermodynamic values. K. Ueno. *J. Chem. Soc. Japan*, **62**, 990–994 (1941).—In the previous works of this series, the vapour press. of solid halides was detd. by Knudsen's effusion method by applying a microbalance which was made of duralumin, and sufficiently accurate results were obtained. The present paper deals with the determination of the vapour press. of solid oxides, WO_3, MoO_3, CdO and TeO_2, using the same app. as in series II. The vapour press. of oxides was detd. between 606° and 1120°C, and the following vapour press. eqs., related with the absolute temp. were calcd. by means of least square, resp.

$$\log p = -\frac{24585.64}{T} + 15.638,$$

$$\log p = -\frac{13902.72}{T} + 13.033,$$

$$\log p = -\frac{13430.86}{T} + 10.366 \text{ and}$$

$$\log p = -\frac{12551.99}{T} + 11.584.$$

From those results were calcd. their thermodynamic values, such as heat of sublimation, free energy change of sublimation and entropy change of sublimation. Author.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY
(CONTACT CATALYSIS)

The action of ultrasonic waves on colloidal solution of sodium oleate. H. Hirata and T. Azami. *Bull. Kiriu Tech. College*, 33–44 (1941).—The changes of viscosity, pH, refractive index and density of concd. aq. solns. of sodium oleate under the irradiation of powerful ultrasonic waves are measured. By the discussion of the results, the following conclusion is obtained. There are two stages in the course of the action.

In the first stage the disintegration of large particles and amorphous micelles of sodium oleate occurs and then, the formation of crystalline micelles takes place in the next stage. Authors.

On the sedimentation volume. K. Suzuki. *J. Chem. Soc. Japan*, 62, 888–895 (1941).—The sedimentation volumes of various kinds of hydrophile powders (e.g. ZnO) and of hydrophobe powders (e.g. ZnS) in C_6H_6, $C_6H_5NO_2$ and C_2H_5OH were measured. Such a measurement serves to estimate the oxidation degree of iron sulphide by ignition. It is experimentally proved that the amount of the particles in the soln. adsorbed on the surface of a powder can be calcd. from the observed value of the sedimentation volume. J. C. L.

Polarity of molecules and their adsorption. The adsorption of isomeric bisubstituted benzenes. B. Tamamushi. *Sc. P.*, 38, 446–454 (1941).—The adsorptions of isomeric bisubstituted benzenes (o- and m-nitrophenol, o- and m-nitraniline and m- and p-dinitrobenzene) by aluminium oxide in benzene on one hand and by charcoal in methyl alcohol on the other, were measured and compared. In the case of nitrophenol as well as nitraniline, the meta-isomer is adsorbed more strongly by aluminium oxide in benzene, while it is adsorbed less strongly by charcoal in methyl alcohol than the ortho-isomer. This is in agreement with the other exptl. results so far obtained. A more polar solute, here the meta-isomer, is adsorbed more strongly by a polar adsorbent, here aluminium oxide, in a more apolar medium, here benzene, than by a more apolar adsorbent, here charcoal, in a more polar medium, here methyl alcohol. In the case of dinitrobenzene, the para-isomer with a smaller dipole moment is adsorbed more strongly by the apolar adsorbent, charcoal, in the polar medium, methyl alcohol, than the meta-isomer with a greater dipole moment, which is in accordance with the other experimental results. This order of adsorption is, however, not reversed when they are adsorbed by aluminium oxide in benzene. This anomaly will be explained, if one takes in account the solubility relation of these isomers in benzene. The meta-isomer, in spite of its greater polarity, is really much more soluble in benzene and accordingly less strongly adsorbed by aluminium oxide than the paraisomer. In spite of some complications, the importance of the polarity of molecules, including those of adsorptive, adsorbent and adsorption medium, in determining the order of adsorption is indicated. J. C. L.

Simple apparatus for the measurement of surface pressure. T. Sasaki. *J. Chem. Soc. Japan*, 62, 796–801 (1941).—A simple app. was constructed for the measurement of the surface press. by means of a vertical glass plate method which is based on the principle of Wilhelmy balance for the measurement of surface tension of liquid. The main part of the app. consists of a vertical glass plate with a glass hook, which takes place of a platinum ring in du Noüy's tensiometer. Thus the app. is simpler than that of Harkins' based on the same principle using a chem. balance instead of a torsion balance. Press.-area curve was detd. by this method for the monolayer of stearic acid on water which shows the same compressibility of the film and the same limiting area per molecule as was detd. by the other methods. This method is highly recommended for the measurement of surface press. chiefly because the whole app. can be constructed cheaply and the exptl. operation is also very simple. Author.

Influence of sorption on the electric conductivity of pulverized metals. I. O. Kimura. *Bull. C. S. J.*, 16, 378–381 (1941).—The electric conductivity of such pulverized metals as Pt, Au, Ni, Co, Cu, and Ag has been measured in the atm. of hydrogen. The effect of hydrogen on the conductivity is characteristic for each metal, and can be

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classified into three types :—1) The conductivity increases as the hydrogen press. rises :—Pt. 2) The conductivity decreases as the hydrogen press. rises :—Ni, Co, Cu, and Ag. 3) No effect :—Au. In the case of nickel, more detailed observations were carried out as regards the oxidation and reduction velocities, the relation between the current and the voltage both in the case of oxidized and reduced nickel, and finally the relation between the conductivity and the hydrogen press. Author.

Studien über oxydationszersetzung des methans. T. Ogura. *Bull. C. S. J.*, **16**, 262–367 (1941).—Diese Abhandlung ist die Resultate der Untersuchungen über die Reaktionen des Methans, des Hauptbestandteils des formosaischen Naturgases, welche es mit Wasserdampf, Sauerstoff und Kohlendioxyd zur Gewinnung des Wasserstoffs durch Oxydationszersetzungen entfaltet. Gleichgewichtskonstanten dieser Reaktionen, insbesondere der Einfluss der Wasserdampfmenge auf Methan - Wasserdampf - Reaktionen und die Veränderung der Bestandteile des Reaktionsgases sind in Nomogram am Anfang der Abhandlung angegeben. Die oben erwähnten drei Reaktionen haben manches gemein an Reaktionsmechanismus und Katalysator. Zur Verfolgung des Katalysators habe ich verschiedene Experimente über Methan-Wasserdampf-Reaktionen angestellt. Ich bin der Meinung, dass die erhaltenen Resultate auch auf die Oxydationszersetzung des Methans verwenden lasse. Ausser Katalysator habe ich auch die Einflüsse von Temperatur, Druck und Mischungsverhältnis untersucht. Die Ergebnisse über Katalysatoren bei der Oxydationszersetzung lassen sich folgendermasser zusammenfassen. (1) Katalysatoren sind notwendig zur Oxydationszersetzung des Methans durch Wasserdampf, Sauerstoff und Kohlendioxyd, Nickel ist bei Wasserdampf-Reaktionen am wirksamsten, aber für die Sauerstoff- und Kohlendioxyd Reaktionen bewährt sich Kobalt am besten. (2) Zusatz einer passenden Menge von Promotor befördert die katalytische Wirkung. Als Promotor empfehle ich passende Menge Alumina. (3) Vermögen des Katalysators wird durch Gebrauch eines Trägers gesteigert, wobei ein passender Konzentrationsgrad des Metalls eine Rolle spielt. Kaolin ist der beste Träger. (4) Niederschlagskatalysator wird in seiner Wirkung durch Röstungs- und Reduktionstemperatur beherrscht. Niedrige Temperatur ist in beiden Fällen immer wünschenswert. (5) Zusatz einer kleinen Menge Alkali beeinträchtigt zwar das Vermögen nicht, er verkürzt aber die Lebensdauer des Katalysators. (6) Existenz einer kleinen Menge Schwefel hat keinen Einfluss auf das Vermögen. Die Bildung des Silikats und Aluminats beeinträchtigt bei niedriger Temperatur die Wirkung. (7) Zusatz einer mässigen Menge Alkali und Alkalierde ist von schädlichem Einfluss. (8) Kontaktdauer ist zwischen 10 und 30 Sekunden. Verminderung des Drucks fördert die Reaktion. Als Beispiel habe ich Methan-Wasserdampf - Reaktion studiert. Steigerung der Reaktionstemperatur befördert die Reaktionen, sie verursacht aber eine Verwandlung der Reaktionsform. Die Bildung des Kohlenoxyd tritt natürlich bei höherer Temperatur ein, bei niederer Temperatur kann man sie durch Zusatz von Stickstoffhaltige Verbindungen erzeugen. Veränderung im Mischungsverhältnis verwandelt auch Reaktionsarten. Ueberschuss vom Wasserdampf gibt Kohlendioxyd. Insbesondere sind Veränderungen im Mischungsverhältnis wesentliche Ursachen einer Verwandlung der Reaktionsarten bei Methan - Sauerstoff - Reaktionen. Wenn die Menge des Sauerstoffs grösser ist, so findet keine Oxydationszersetzung statt, sondern eine Verbrennungsreaktion. Zum Schluss der Abhandlung habe ich die Resultate der Reaktionen des Methans mit Luft-Wasserdampf und Kohlendioxyd-Wasserdampf in einigen Tafeln zusammengestellt, ohne weiter auf die technischen Fragen einzugehen. Author.

Physicochemical investigation of the synthesis of benzin. IV. On the velocity of adsorption of hydrogen on

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reduced cobalt. S. Kodama, S. Matsumura and K. Tarama. *J. Soc. Chem. Ind. Japan*, 44, 823-825 (1941).—The velocity of adsorption of hydrogen on reduced cobalt is detd. The value x, volume of hydrogen adsorbed during t sec is given by the eq., $t/x=t/A+1/A^2k$. This eq. was obtained by the present writers under the assumption that the adsorption of hydrogen is atomic. The const. A calcd. from the exptl. results at various temps. have been scattered in wide range and the value K which should satisfy the Arrhenius eq. on uniform catalyst surface, was found not to stand in a close relation with temp. These facts lead to the conclusion, that there are several centers with different activities on the surface of the cobalt and the centers having relatively higher activity play an important role at lower temps., the observed adsorption being chiefly due to such centers, while at higher temps. the adsorption on centers with lower activity predominates in exptl. region. Authors.

Physico-chemical investigations on catalytic mechanism. II. Note on the Fischer-Tropsch synthesis of hydrocarbons with special reference to its reaction mechanism. S. Hamai. *Bull. C. S. J.*, **16**, 213-228 (1941).—The present paper is a detailed formulation and the discussions of the mech. already proposed in the previous paper (I) (*J. Chem. Soc. Japan*, **62**, 516-518, (1941)). The related phenomena are also discussed in the light of various extl. observations. They may be summarized as follows: 1) Introductory remarks for the Fischer-Tropsch reaction in connection with various mechs. so far proposed are presented briefly. 2) The proposed mech. is presented and discussed in detail. 3) The role of CH_2 in hydrocarbon chemistry in general is stressed especially in connection with the Fischer-Tropsch reaction mech. 4) Approximate values of the activation energies for the reactions involved in the synthesis are presented and discussed in correlation with adsorption. 5) The aspect of polymerization process is discussed, and the question of surface migration is correlated with the polymerization reaction. 6) Adsorption and catalytic activity involved in the synthesis are discussed in the light of the author's desorption expt. 7) The proposed mech. is also applied to Fe type catalyst and discussed. 8) Various pretreatment effects on the catalytic activity are discussed in the light of his exptl. evidences. Author.

On the relation between the α-γ transformation of an Fe-Ni alloy and the velocity of catalytic decomposition of ammonia gas when this alloy is used as catalyst. I. T. Koyano and R. Ito. *J. Chem. Soc. Japan*, **62**, 984-989 (1941).—Using an Fe-Ni alloy (Ni 10%) as catalyst the decompn. velocity of ammonia gas was measured at each temp. between 500°-700°. It was observed that the velocity const. coincided within the range of error at each temp., whether ascending or descending at various rates. It was also observed that these consts. showed an abrupt change at the temp. at which α-γ transformation might begin under ascending condition which might be expected from those expts. concerning "non-surface phenomena", while those showed the histeresis is phenomena which resulted from the incoincidence between ascending and descending sides. On the basis of these results the dependence of catalytic activity on lattice structure and the α-γ transformation in the surface are discussed. Authors.

Preparation of butadiene from 1, 3-butylene glycol by dehydration in vapour phase. IX-X. Stability of butadiene in the presence of various dehydrating catalysers. H. Nagai. *J. Soc. Chem. Ind., Japan*, 44, 973-979 (1941).—The content of butadiene in the gas evolved by the dehydration of 1,3-butylene glycol is largely influenced by the properties of the catalyser used, especially by its action on butadiene. The author accordingly experi-

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mented on the stability of butadiene in the presence of various dehydrating catalysers. The gaseous butadiene was conducted into the reaction tube contg. the catalyser heated at the reaction temp. in the electric furnace. It has been found that in the presence of the mixed catalyser of kaolin-Fe_2O_3-KOH butadiene is polymerized into oily substances on one hand and decomposed into the substances of lower molecular wts. on the other. These reactions become remarkable with the elevation of temp., but above 350°C the decompn. takes place to a greater extent than the polymerization, and so the formation of oily substances is at maximum at that temp. In the presence of the mixed catalyser of kaolin and phosphoric acid, however, butadiene is very stable at temperature below 350°C, and above that temp. polymerization and decompn. take place simultaneously, while at higher temp. the polymerization preponderates, resulting in the formation of oily substances.

Author.

The influence of nickel bromide and various solvents on the addition of hydrogen bromide to stylene in the presence of reduced nickel. M. Takebayashi. *J. Chem. Soc. Japan*, 62, 1107–1112 (1941).—The author studied the action of HBr upon stylene in the presence of reduced nickel or nickel bromide in various solvents, and compared the results with that in the presence of oxygen or peroxide. The addition reaction which produces α-phenyl-ethyl bromide is normal; the addition reaction which produces β-phenyl-ethyl bromide is abnormal. The compn. of the addition products, α- and β-bromides, was detd. by the extent of hydrolysis and the refractive indices. In the absence of solvents, the reaction proceeded almost normal, even when the catalysts were present. In the presence of solvents, the results were not simple. In benzene or carbon tetrachloride soln., the normal addition reaction predominated, and the effects of reduced nickel and of oxygen or peroxide on the direction of the addition reaction were very slight. In ligroin soln., the abnormal addition was remarkably promoted by oxygen or peroxide, while not so conspicuously by reduced nickel. The influence of nickel bromide was examd. in ligroin soln. It was found that nickel bromide accelerated the normal addition reaction, interrupting the effects of the metal and oxygen or peroxide. The weakness of the effect of reduced nickel is presumed to be due to the nickel bromide produced from Ni and HBr.

Author.